methane, but complete structural assignments could not be made for these compounds.

Registry No.—**1a**, 34839-56-0; **1b**, 34839-57-1; **4**, 519-73-3; **5a**, 5467-21-0; **5b**, 34823-77-3; **6a**, 34823-78-4; **6b**, 34823-79-5; **7a**, 34823-80-8; **8b**, 34823-81-9; methyl carbazate, 6294-89-9; methyl 3-tritylcarbazate, 34823-82-0; phenyl carbazate, 20605-43-0; phenyl 3-tritylcarbazate, 34823-83-1.

Acknowledgment.—We thank Professor Glen A. Russell for helpful discussions of this work.

Strained Ring Systems. XII.[1a] The Synthesis of Several Dimethyl Δ^1-Cycloalkene-1,2-dicarboxylates and Certain 4-Substituted Bicyclo[2.1.0]pentane-1-carboxylic Acids

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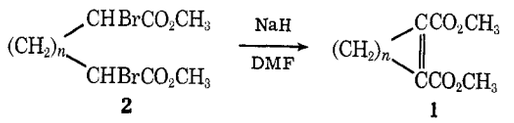
A one-step synthesis of dimethyl Δ^1-cycloalkene-1,2-dicarboxylates (**1**) (cyclobutene to cycloheptene) from the corresponding dimethyl α,α'-dibromoalkanedicarboxylates is given. While dimethyl Δ^1-cyclopropene-1,2-dicarboxylate (**1a**) is believed produced from the reaction of dimethyl α,α'-dibromoglutarate (**2a**) and potassium *tert*-butoxide, cis addition of an alcohol to **1a** proceeds to yield the dimethyl 1-alkoxycyclopropane-*cis*-1,2-dicarboxylates **4** and **5**. Reaction of dimethyl Δ^1-cyclobutene-1,2-dicarboxylate (**1b**) with diazomethane followed by photolysis of the product pyrazoline yields dimethyl bicyclo[2.1.0]pentane-1,4-dicarboxylate (**6**). Through standard reaction sequences **6** is converted to bicyclo[2.1.0]pentane-1,4-dicarboxylic acid, 4-carbomethoxy-, 4-carbamyl-, and 4-cyanobicyclo[2.1.0]pentane-1-carboxylic acids. Bicyclo[2.1.0]pentane-1-carboxylic acid was prepared by hydrolysis of its methyl ester.

We recently reported the preparation of several 5-substituted bicyclo[3.1.0]hexane-1-carboxylic acids[2] using standard reaction sequences for modifying the carboxylic acid group[3-6] of 5-carbomethoxybicyclo-[3.1.0]hexane-1-carboxylic acid. We wish to report in this paper the synthesis of certain 4-substituted bicyclo[2.1.0]pentane-1-carboxylic acids which were required to determine the effect of bridgehead substituent groups on the acidity of bicyclo[*n*.1.0]alkane-1-carboxylic acids.

The synthetic approach to dimethyl bicyclo[2.1.0]-pentane-1,4-dicarboxylate (**6**) which appeared most promising was the addition of diazomethane to dimethyl Δ^1-cyclobutene-1,2-dicarboxylate (**1b**) followed by photolytic decomposition of the resulting pyrazoline, similar to the reported method used for preparing methyl bicyclo[2.1.0]pentane-1-carboxylate.[7,8]

Synthesis of Dimethyl Δ^1-Cycloalkene-1,2-dicarboxylates.—The reported procedures for the preparation of diester **1b** or its diacid are quite lengthy[9,10] and involve cyclobutane-1,2-dicarboxylic acid as an intermediate. By analogy to the four-membered ring formation in the reaction of dimethyl α,α'-dibromoadipate (**2b**) with cyanide ion, which is part of the sequence leading to cyclobutane-1,2-dicarboxylic acid,[11] it appeared that reaction of **2b** with 2 equiv of base should accomplish both cyclization and vicinal elimination of hydrogen bromide to yield **1b** directly.

Our first attempt at such a reaction proved fruitful. When **2b** was allowed to react with 2 equiv of sodium hydride in dimethylformamide, **1b** was isolated in 68%



2 **1**

a, $n = 1$ **d**, $n = 4$
b, $n = 2$ **e**, $n = 5$
c, $n = 3$ **f**, $n = 6$

yield. Since this procedure offered a simple, reasonably direct synthesis of **1b**, we decided to examine its possible generality for the synthesis of dimethyl Δ^1-cycloalkene-1,2-dicarboxylates. A series of dimethyl α,α'-dibromoalkanedicarboxylates (**2**) derived from glutaric acid through sebacic acid[12a] were prepared and allowed to react with sodium hydride in dimethylformamide; the conditions and results are given in Table I.[12b,13,14]

The reactions of **2a–d** proceeded smoothly at ice-bath or room temperature. However, the reactions with **2e** and **2f** were quite slow even at room temperature. While this procedure gives good yields of **1b–d** and an acceptable yield of **1e**, none of the desired products **1a** or **1f** were obtained from **2a** and **2f**, respectively.

(1) (a) For paper XI in this series, see R. N. McDonald, D. G. Frickey, and G. M. Muschik, *J. Org. Chem.*, **37**, 1304 (1972). (b) NDEA Fellow, 1968–1970; NSF Trainee, 1970–1971.

(2) R. N. McDonald and R. R. Reitz, *J. Org. Chem.*, **35**, 2666 (1970).

(3) F. W. Baker and L. M. Stock, *ibid.*, **32**, 3344 (1967).

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(5) C. F. Wilcox and C. Leung, *J. Org. Chem.*, **33**, 877 (1968).

(6) C. F. Wilcox and J. S. McIntyre, *ibid.*, **30**, 777 (1965).

(7) W. G. Dauben and J. R. Wiseman, *J. Amer. Chem. Soc.*, **89**, 3545 (1967).

(8) P. G. Gassman and K. T. Mansfield, *J. Org. Chem.*, **32**, 915 (1967).

(9) F. B. Kipping and J. J. Wren, *J. Chem. Soc.*, **51**, 1537 (1929).

(10) W. H. Perkins, *ibid.*, **65**, 950 (1894).

(11) R. C. Fuson and T. Y. Kao, *J. Amer. Chem. Soc.*, **51**, 1537 (1929).

(12) (a) The procedure used in the synthesis of esters **2** followed that reported for the preparation of **1b**: E. Buchman, A. Reims, T. Skei, and M. Schlatter, *ibid.*, **64**, 2697 (1942); P. C. Guha and D. K. Sankaran, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 623. (b) A similar procedure for the synthesis of **1c** has been reported by D. C. Owsley and J. J. Bloomfield, *Org. Prep. Proced. Int.*, **3**, 61 (1971).

(13) (a) Small amounts of the diacids of **1b**, **1c**, and **1d** have been obtained from base hydrolyses of the corresponding esters of **2**; see A. Hassell and C. K. Ingold, *J. Chem. Soc.*, 1465 (1926), and F. R. Goss and C. K. Ingold, *ibid.*, 1471 (1926). (b) **1b** has been obtained in low yield from the dehalogenation of dimethyl *cis*-1,2-dihalocyclobutane-1,2-dicarboxylate (X = Cl, Br) with $Ni(CO)_4$; see H.-D. Scharf and F. Korte, *Chem. Ber.*, **98**, 764 (1965).

(14) A reported attempt at formation of Δ^1-cyclobutene-1,2-dicarboxylic acid by a Ramberg–Bachlund reaction was unsuccessful; see T. Bacchetti and A. Arnaboldi, *Atti Accad. Naz. Lincei, Rend., Cl. Sci. Fis., Mat. Natur.*, **15**, 75 (1953); *Chem. Abstr.*, **49**, 2301*b* (1955).

TABLE I
RESULTS OF CYCLIZATION–ELIMINATION REACTION

Dibromo diester 2	Reaction time, hr	Temp, °C	Yield of 1,[a] %
a (glutarate)	1.5	0	0[b]
b (adipate)	4.0	25	68
c (pimeltate)	1.5	0	69
d (suberate)	3.0	0	71
e (azelate)	36	25	21
f (sebacate)	36	25	0

[a] None of the isomeric dimethyl cycloalkene-1,2-dicarboxylates were found. [b] Longer reaction times and increased temperatures gave only increased amounts of polymeric material.

Although little reaction was observed between **2f** and sodium hydride in dimethylformamide, the results obtained from reactions of **2a** with this and another basic system deserve special comment. Reaction of **2a** with 2 equiv of sodium hydride in dimethylformamide at 0°, after the steady evolution of hydrogen had ceased, gave a 77% yield of dimethyl 1-bromocyclopropane-*cis*- and -*trans*-1,2-dicarboxylate (**3**) in a ratio of 1:3, respectively. The structural assignments of the two isomers of **3** were based on analysis of their nmr spectra when compared to those of **4** and **5**.

Reaction of **2a** with 2 equiv of potassium *tert*-butoxide in *tert*-butyl alcohol gave two products, dimethyl 1-*tert*-butoxy- (**4**, 46%) and dimethyl 1-methoxycyclopropane-*cis*-1,2-dicarboxylate (**5**, 9%). Both **4** and **5** exhibited almost superimposable ABC multiplets for the ring protons in their nmr spectra, which established their structures as having the same geometric relationship of the carbomethoxy groups (probably cis). This ABC multiplet portion of the nmr spectra was used to assign structures to the cis and trans isomers of **3**.

The cis relationship of the carbomethoxy groups in **4** and **5** was verified by hydrolysis of a mixture of **4** and **5** to their respective dicarboxylic acids, formation of the two anhydrides (ir absorptions at 1850 and 1780 cm^{-1}) with acetic anhydride, and hydrolysis with warm water to regenerate the diacids. Reaction of these two diacids with diazomethane reformed **4** and **5**.

Reaction of **2a** with 1 equiv of potassium *tert*-butoxide in *tert*-butyl alcohol produced a mixture containing *cis*- and *trans*-**3** along with some **4** and **5**. Similar reaction with a mixture of *cis*- and *trans*-**3** produced a mixture of **4** and **5**.

The observation of **3** as the primary product from the reaction of **2a** with potassium *tert*-butoxide rules out nucleophilic displacement of bromide by the alkoxide followed by cyclization as the mechanism involved in the formation of **4** and **5**. A more reasonable mechanism for producing **4** and **5** would be a stepwise 1,3 elimination from **2a** to **3**, vicinal elimination in **3** to yield the highly reactive intermediate dimethyl Δ^1-cyclopropene-1,2-dicarboxylate (**1a**), followed by cis addition of the alcohol to the strained double bond.[15] The presence of methanol in these reactions is probably due to transesterification of the methyl ester groups.

Synthesis of Certain 4-Substituted Bicyclo[2.1.0]pentane-1-carboxylic Acids.—Utilizing the synthetic approach already outlined for the synthesis of dimethyl bicyclo[2.1.0]pentane-1,4-dicarboxylate (**6**), **1b** was allowed to react with diazomethane to give pyrazoline **7** in 92% yield.[16] Photolysis of **7** in ether using a Hanovia 450-W (type L) lamp and a Corex filter in a quartz immersion well gave **6** in 51% yield. With no filter the photolysis proceeded much faster but more polymeric material was obtained along with a reduced yield of **6**. Use of a Pyrex filter slowed the reaction considerably.

From **6** several 4-substituted bicyclo[2.1.0]pentane-1-carboxylic acids were prepared by standard routes,[2-6] as shown in Scheme I. Diester **6** was saponified completely to diacid **8** and partially to half-ester **9**. Half-ester **9** was converted to carbamyl ester **10**, which was dehydrated to cyano ester **11**. Esters **10** and **11** were

SCHEME I

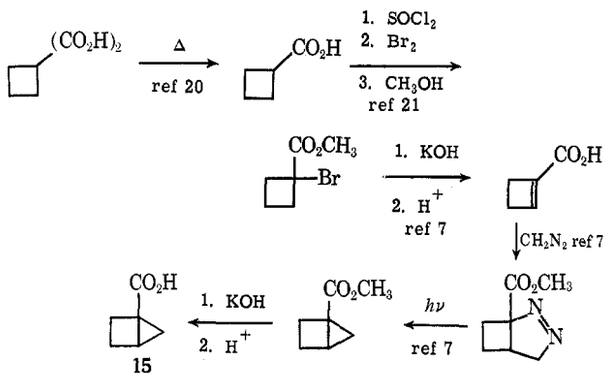
(15) K. B. Wiberg, R. K. Barnes, and J. Albin [*J. Amer. Chem. Soc.*, **79**, 4994 (1957)] suggested a similar addition of *tert*-butyl alcohol to ethyl Δ^1-cyclopropenecarboxylate to account for the formation of ethyl *trans*-2-*tert*-butoxycyclopropanecarboxylate from ethyl *trans*-2-bromocyclopropanecarboxylate.

(16) Addition of diazomethene to **1c** was slow at 0° and required only 24 hr at room temperature to give a 90% yield of the pyrazoline, which was photolyzed to dimethyl bicyclo[3.1.0]hexane-1,5-dicarboxylate (see Experimental Section). However, no pyrazoline formation was observed with **1d** even after several days at room temperature with excess diazomethane.

hydrolyzed to their respective acids, **12** and **13**. A Hunsdiecker reaction[17] using mercuric oxide and bromine on half-ester **9** did not produce the desired compound, methyl 4-bromobicyclo[2.1.0]pentane-1-carboxylate, the bicyclo[2.1.0]pentane nucleus being apparently unstable to these reaction conditions.[18,19]

Preparation of methyl bicyclo[2.1.0]pentane-1-carboxylate (**14**) was accomplished according to the procedures of Dauben[7] and Gassman,[8] and is outlined in Scheme II[20,21] starting from commercially available

SCHEME II



cyclobutane-1,1-dicarboxylic acid. Ester **14** was hydrolyzed to bicyclo[2.1.0]pentane-1-carboxylic acid (**15**).

Experimental Section[22]

General Procedure for Synthesis of Dimethyl α,α′-Dibromoalkanedicarboxylates (2).—The method applied to the conversion of adipic acid to dimethyl α,α′-dibromoadipate[12] of stepwise reactions of the diacid with thionyl chloride, bromine, and methanol was employed.

Dimethyl α,α′-Dibromoglutarate (2a).—Glutaric acid (50 g) produced after distillation [120° (0.01 mm)] 126 g (90%) of **2a** as a viscous liquid: ir (thin film) 1740 cm^{-1} (C=O); nmr (CCl_4) τ 5.33–5.75 (m, $C_\alpha H$'s, 2), 6.15 (s, OCH_3, 6), 7.05–7.45 (m, $C_\beta H_2$'s, 2).

Dimethyl α,α′-Dibromoadipate (2b).—Adipic acid (220 g) produced after distillation [175–180° (0.2 mm)] 450 g (90%) of **2b**: ir (thin film) 1730 cm^{-1} (C=O); nmr (CCl_4) τ 5.5–5.9 (m, $C_\alpha H$'s, 2), 6.20 (s, OCH_3, 6), and 7.5–8.0 (m, $C_\beta H_2$'s, 4).

Dimethyl α,α′-Dibromopimelate (2c).—Pimelic acid (25 g) produced after distillation [130–140° (0.01 mm)] 52.5 g (96%) of viscous, liquid **2c**: ir (thin film) 1740 cm^{-1} (C=O); nmr (CCl_4) τ 5.33–5.74 (m, $C_\alpha H$'s, 2), 6.15 (s, OCH_3, 6), 7.6–8.15 [m (shape of triplet centered at τ 7.95, J = 6.5 Hz), $C_\beta H_2$'s, 4], and 8.15–8.70 (m, $C_\gamma H_2$, 2).

Dimethyl α,α′-Dibromosuberate (2d).—Suberic acid (25 g) gave after distillation [110–120° (0.01 mm)] 48.0 g (93%) of yellowish, viscous **2d**: ir (thin film) 1740 cm^{-1} (C=O); nmr (CCl_4) τ 5.73 [t center (J = 7.0 Hz), $C_\alpha H$'s, 2], 6.18 (s, OCH_3, 6), 7.6–8.2 (m, $C_\beta H_2$'s, 4), and 8.2–8.7 (m, $C_\gamma H_2$'s, 4).

Dimethyl α,α′-Dibromoazelate (2e).—Azelaic acid (50 g) produced after distillation [120–130° (0.01 mm)] 92.1 g (92%) of viscous **2e**: ir (thin film) 1740 cm^{-1} (C=O); nmr (CCl_4) τ 5.87 [t center (J = 7.4 Hz), $C_\alpha H$'s, 2], 6.21 (s, OCH_3, 6), 7.6–8.3 (m, $C_\beta H_2$'s, 4), and 8.3–8.8 (m, $C_\gamma H_2$'s and $C_\delta H_2$'s, 6).

Dimethyl α,α′-Dibromosebacate (2f).—Sebacic acid (50 g) gave after distillation [120–130° (0.01 mm)] 89.0 g (91%) of viscous **2f**: ir (thin film) 1740 cm^{-1} (C=O); nmr (CCl_4) τ 5.87 [t center (J = 7.2 Hz), $C_\alpha H$'s, 2], 6.21 (s, OCH_3, 6), 7.6–8.3 (m, $C_\beta H_2$'s, 4), and 8.3–8.8 (m, $C_\gamma H_2$'s and $C_\delta H_2$'s, 8).

Dimethyl Δ¹-Cyclobutene-1,2-dicarboxylate (1b). General Procedure.[23,24]—To 50.0 g (150 mmol) of dimethyl α,α′-dibromoadipate in 350 ml of dry dimethylformamide, cooled to ice-bath temperature, was added 13.2 g (310 mequiv) of sodium hydride (57% in mineral oil). After a few minutes of vigorous stirring, the ice bath was removed and the stirring was continued until the evolution of hydrogen had ceased (about 4 hr) and the mixture had taken on a slight yellow color. If the evolution of hydrogen became too rapid, since the reaction was exothermic, a steady evolution of hydrogen could be reestablished by control with the ice bath. To the reaction mixture was added 600 ml of ether. The precipitate of sodium bromide and unreacted sodium hydride could be removed by filtration. The filtrate was then extracted with four 150-ml portions of brine to remove the DMF. The aqueous layers obtained were washed several times with additional ether. The ether solutions were combined and dried ($MgSO_4$). The ether was then removed at reduced pressure leaving a reddish-brown liquid residue.

This liquid was trap to trap distilled [65–100° (0.1 mm)], giving a product composed mainly of white solid. This crude distillate was fractionated using an 8-in. Vigreux column with collection of the lower boiling fraction [60–80° (1 mm)] giving 17.5 g of product. Analysis of glpc on a 6 ft × 0.25 in. 10% QF-1 on Anachrom ABS column showed one main component and about 15% impurity. Correction for impurities gave a yield of 68%. The ir[13b] and nmr spectra[25] agreed with those reported. The product could be further purified by recrystallization from ether–hexane, mp 44–45° (lit.[13b] mp 45°).

Dimethyl Δ¹-Cyclopentene-1,2-dicarboxylate (1c).—Dimethyl α,α′-dibromopimelate (20.0 g, 60.5 mmol) and 5.5 g (131 mequiv) of sodium hydride (57% in oil) in 250 ml of dry DMF were stirred at ice-bath temperature for 1.5 hr until hydrogen evolution had ceased and the mixture had become yellowish. After work-up and trap-to-trap distillation [100° (0.01 mm)], 7.73 g of product was obtained. Glpc analysis showed the presence of 9% impurities, giving a corrected yield of 69% of **1c**: ir (thin film) 1725 (C=O) and 1650 cm^{-1} (C=C); nmr (CCl_4) τ 6.30 (s, OCH_3, 6), 7.29 [t (complex) (J = 7.0 Hz), allylic methylene protons, 4], and 7.95 [q (complex) (J = 7.0 Hz), central methylene protons, 2]. An analytical sample was collected by glpc and trap to trap distilled.

Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.30; H, 6.95.

Dimethyl Δ¹-Cyclohexene-1,2-dicarboxylate (1d).—Dimethyl α,α′-dibromosuberate (48 g, 133 mmol) and 15 g (313 mequiv) of sodium hydride (57% in oil) in 300 ml of dry DMF were stirred at ice-bath temperature for 3 hr (hydrogen evolution slowed considerably after 2.5 hr). After work-up and trap-to-trap distillation [100° (0.01 mm)], 18.73 g (71%) of **1d** was obtained which was "pure" as judged from its nmr spectrum: ir (thin film) 1740 (C=O) and 1650 cm^{-1} (C=C); nmr (CCl_4) τ 6.33 (s, OCH_3, 6), 7.5–8.0 [m (A_2B_2 pattern with a characteristic peak at τ 7.71), allylic methylene protons, 4], 8.0–8.5 [m (A_2B_2 pattern with a characteristic peak at τ 8.33), central methylene protons, 4]. An analytical sample was collected by glpc and trap to trap distilled.

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.73; H, 7.28.

Dimethyl Δ¹-Cycloheptene-1,2-dicarboxylate (1e).—Dimethyl α,α′-dibromoazelate (20.0 g, 53.5 mmol) and 4.52 g (107 mequiv) of sodium hydride (57% in oil) in 200 ml of dry DMF were stirred

(17) J. S. Meek and D. T. Osuga, *Org. Syn.*, **43**, 9 (1963).
(18) R. Criegee and R. Rimmelin, *Chem. Ber.*, **90**, 414 (1957).
(19) R. T. LaLonde, *J. Amer. Chem. Soc.*, **87**, 4217 (1965).
(20) J. Cason and F. Allen, *J. Org. Chem.*, **14**, 1036 (1949).
(21) A. Cambell and H. N. Rydon, *J. Chem. Soc.*, 3002 (1953).
(22) All melting points were determined on a Kofler hot stage. Boiling points are uncorrected. "Boiling points" for trap-to-trap distillations are pot temperatures. Infrared and nmr spectra were obtained on a P-E 137 spectrophotometer and on Varian A-60 and T-60 spectrometers. Gas chromatographic analyses were performed using a F & M Model 500 temperature-programmed gas chromatograph. Near infrared spectra were obtained on a Cary 14 spectrophotometer. Microanalyses were done by Atlantic Microlabs, Inc., Atlanta, Ga. Mass spectra were determined on a MS-9 spectrometer.

(23) The authors wish to thank Mr. David Cole for repetition of this experiment and consistently obtaining the higher yield reported here. R. N. McDonald and R. R. Reitz [*Chem. Commun.*, 90 (1971)] previously reported the yield of **1b** to be 48%.

(24) Dr. J. Bloomfield has informed us that when this reaction is run on a 1-mol scale a large exotherm is observed. A large flask and cooling should be employed.

(25) D. Seebach, *Chem. Ber.*, **97**, 2953 (1964).

for 24 hr at room temperature. After work-up and trap-to-trap distillation [110° (0.01 mm)], 2.42 g (21%) of **1e** was obtained pure by nmr and glpc: ir (thin film) 1725 (C=O) and 1640 cm^{-1} (C=C); nmr (CCl_4) τ 6.33 (s, OCH_3, 6), 7.4–7.6 (m, allylic methylene protons, 4), and 8.2–8.6 (m, central methylene protons, 6). An analytical sample was collected by glpc and trap to trap distilled.

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.55; H, 7.78.

Reactions of Dimethyl α,α'-Dibromoglutarate (2a) with Strong Bases. A. With Sodium Hydride.—**2a** (10.0 g, 31.4 mmol) and 2.5 g (58 mequiv) of sodium hydride (57% in oil) in 125 ml of dry DMF were stirred at ice-bath temperature for 1.5 hr (hydrogen evolution had ceased). After work-up and trap-to-trap distillation [90° (0.01 mm)], 5.80 g (77%) of a colorless liquid product was obtained. Nmr spectral and glpc analysis showed this to be a 1:3 mixture of the dimethyl esters of 1-bromo-*cis*- and -*trans*-cyclopropane-1,2-dicarboxylic acid (**3**). Glpc collection gave pure samples of each diester.

The data on *cis*-**3** are as follows: ir (thin film) 1740 (C=O) and 1025 cm^{-1} (cyclopropyl CH_2); nmr (CCl_4) τ 6.27 (s, OCH_3, 3), 6.32 (s, OCH_3, 3), 7.62 [m (four lines), methine proton, 1], 7.93 [m (four lines), ring proton cis to CO_2CH_3's, 1], 8.39 [m (four lines), ring proton trans to CO_2CH_3's, 1], and coupling constants for the ABC pattern J (trans) = 7.0, J (cis) = 9.2, and J (geminal) = −6.0 Hz.

Anal. Calcd for $C_7H_9O_4Br$: C, 35.47; H, 3.83. Found: C, 35.72; H, 3.98.

The data on *trans*-**3** are as follows: ir (thin film) 1730 (C=O) and 1030 cm^{-1} (cyclopropyl CH_2); nmr (CCl_4) τ 6.23 (s, OCH_3, 3), 6.26 (s, OCH_3, 3), 7.48 [m (four lines), methine proton, 1], 7.9–8.3 [m (characteristic peaks at τ 7.96, 8.05, 8.20, and 8.22), methylene protons, 2], and coupling constants for the ABC pattern J (trans) = 7.8, J (cis) = 8.8, and J (geminal) = −6.0 Hz.

Anal. Calcd for $C_7H_9O_4Br$: C, 35.47; H, 3.83. Found: C, 35.80; H, 3.85.

B. With 2 Equiv of Potassium *tert*-Butoxide.—A solution of potassium *tert*-butoxide in *tert*-butyl alcohol [prepared from 5.0 g (0.128 g-atom) of potassium and 100 ml of *tert*-butyl alcohol] was added dropwise over a 1-hr period to 20.0 g (62.9 mmol) of **2a** in 60 ml of *tert*-butyl alcohol. A precipitate of potassium bromide formed immediately. After addition of the base was complete, the reaction was stirred for an additional 0.5 hr at room temperature. Ether (300 ml) was added and the ether solution was washed with three 200-ml portions of water, dried ($MgSO_4$), and concentrated. The residue was trap to trap distilled [100° (0.01 mm)] giving 7.73 g of colorless liquid. Glpc analysis on a 10 ft × 0.25 in. 10% Carbowax on Chromosorb W column showed the presence of two components in a ratio of 13:87. These components were preparatively collected and identified.

The first component (8.6%) was assigned the structure of dimethyl 1-methoxy-*cis*-cyclopropane-1,2-dicarboxylate: ir (thin film) 1730 (C=O) and 1030 cm^{-1} (cyclopropyl CH_2); nmr (CCl_4) τ 6.30 (s, OCH_3, 3), 6.33 (s, OCH_3, 3), 6.59 (s, OCH_3, 3), 7.89 [m (four lines), methine proton, 1], 8.23 [m (four lines), CH_2 ring proton cis to CO_2CH_3's, 1], 8.62 [m (four lines), CH_2 ring proton trans to CO_2CH_3's, 1]. The coupling constants for the ABC pattern were J (trans) = 7.5, J (cis) = 10.0, and J (geminal) = −5.4 Hz.

Anal. Calcd for $C_8H_{12}O_5$: C, 51.06; H, 6.42. Found: C, 51.46; H, 6.72.

The second component (46.3%) was assigned the structure of dimethyl 1-*tert*-butoxy-*cis*-cyclopropane-1,2-dicarboxylate: ir (thin film) 1730 cm^{-1} (C=O); nmr (CCl_4) τ 6.35 (s, OCH_3, 3), 6.38 (s, OCH_3, 3), 7.92 [m (four lines), methine proton, 1], 8.25 [m (four lines), CH_2 ring proton cis to CO_2CH_3's, 1], 8.62 [m (four lines), CH_2 ring proton trans to CO_2CH_3's, 1], and 8.76 [s, $OC(CH_3)_3$, 9]. The coupling constants for the ABC pattern were J (trans) = 7.5, J (cis) = 9.5, and J (geminal) = −5.0 Hz.

Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.46; H, 7.97.

C. With 1 Equiv of Potassium *tert*-Butoxide.—A solution of potassium *tert*-butoxide in *tert*-butyl alcohol [prepared from 3.9 g (0.095 g-atom) of potassium and 50 ml of *tert*-butyl alcohol] was added dropwise to 30 g (95 mmol) of **2a** in 30 ml of *tert*-butyl alcohol. The reaction was worked up in the same manner as was the reaction with 2 equiv of base. Trap-to-trap distillation [100° (0.01 mm)] gave 16.9 g of colorless liquid. An nmr spectrum of this crude product showed starting material and several other ester products. These other ester products were identified by glpc analysis by comparison of retention times with those of authentic samples. Glpc analysis using a 6 ft × 0.25 in. 10% DEGS on Anakrom ABS column showed the presence of four peaks with the following retention times and relative percentages: 10.3 (18%), 11.0 (22%), 11.6 (14%), and 13.8 min (46%). These compounds were assigned the structures of the dimethyl esters of 1-methoxy-*cis*-, 1-*tert*-butoxy-*cis*-, 1-bromo-*cis*-, and 1-bromo-*trans*-cyclopropane-1,2-dicarboxylic acids, respectively, from their glpc retention times compared with those of authentic samples.

Reaction of Dimethyl 1-Bromo-*cis*- and -*trans*-cyclopropane-1,2-dicarboxylate with 1 Equiv of Potassium *tert*-Butoxide.—To 1.673 g (7.06 mmol) of dimethyl 1-bromo-*cis*- and -*trans*-cyclopropane-1,2-dicarboxylate (**3**) in 20 ml of *tert*-butyl alcohol was added 0.80 g (7.15 mequiv) of potassium *tert*-butoxide (MSA Research Corp.). A precipitate formed immediately. The reaction was worked up in the same manner as described above, giving 0.7 g of liquid. Glpc analysis showed three main products which were identified, by retention time comparison with authentic samples, as the dimethyl esters of 1-methoxy-*cis*- (38%), 1-*tert*-butoxy-*cis*- (31%), and 1-bromo-*trans*-cyclopropane-1,2-dicarboxylic acids (31%).

1-*tert*-Butoxy-*cis*- and 1-Methoxy-*cis*-cyclopropane-1,2-dicarboxylic Anhydride.—A 1.0-g sample of an 87:13 mixture of the dimethyl esters of 1-*tert*-butoxy-*cis*- and 1-methoxy-*cis*-cyclopropane-1,2-dicarboxylic acids was treated with excess potassium hydroxide in 80% methanol under reflux for 1 hr. Work-up was in the usual manner, giving about 0.2 g of crude diacids, ir (Fluorolube mull) 2400–3400 (acid OH) and 1700 cm^{-1} (C=O). This crude mixture of diacids was allowed to stir at 50° in 15 ml of acetic anhydride for 30 min. The resulting mixture of anhydrides was trap to trap distilled [70–80° (0.01 mm)] giving a small amount of colorless liquid which solidified upon standing: ir (thin film) 1850 and 1780 cm^{-1} (C=O); nmr (CCl_4) τ 6.40 (s, OCH_3), 7.08–7.32 [m (four lines)], 7.7–8.3 (m), and 8.68 [s, $OC(CH_3)_3$]. This mixture of anhydrides was hydrolyzed in warm water and extracted into ether. The ether solution was treated with excess diazomethane in ether, which after concentration, gave the starting methyl esters as shown from nmr spectral comparison.

Dimethyl 2,3-Diazabicyclo[3.2.0]hept-2-ene-1,5-dicarboxylate (7).—An ether solution (800 ml) of diazomethane (prepared from 26 g of *N*-nitroso-*N*-methylurea) and 21.40 g (0.125 mol) of dimethyl Δ^1-cyclobutene-1,2-dicarboxylate was allowed to stand in the refrigerator (0–10°) for 20 hr, after which an nmr spectrum of an aliquot showed no starting material remaining. Excess diazomethane and ether were distilled off and the residue was recrystallized from ether–hexane and sublimed [50° (0.01 mm)], giving 24.87 g (92%) of crystalline **7**: mp 38–39°; ir (thin film) 1740 (C=O) and 1550 cm^{-1} (N=N); nmr (CCl_4) τ 5.18 [q (J = 18 Hz), CH_2N, 2], 6.29 (s, OCH_3 3), 6.34 (s, OCH_3, 3) 6.8–8.7 (complex m, cyclobutane ring protons, 4).

Anal. Calcd for $C_9H_{12}O_4N_2$: C, 50.94; H, 5.70. Found: C, 50.94; H, 5.81.

Dimethyl 2,3-Diazabicyclo[3.3.0]oct-2-ene-1,5-dicarboxylate.—Dimethyl Δ^1-cyclopentene-1,2-dicarboxylate (8.49 g, 46.1 mmol) was allowed to stand in a solution of excess diazomethane in ether in the refrigerator (0–10°) for 3 days, after which time the nmr spectrum showed that about 50% reaction had taken place. After the solution had stood for an additional day at 25°, no starting material remained. The mixture was concentrated and the liquid product was trap to trap distilled [100° (0.01 mm)] giving 9.45 g of colorless liquid that showed about 10% impurity by nmr spectral analysis (90% yield). A second distillation left only 5% impurity: ir (thin film) 1740 (C=O) and 1560 cm^{-1} (N=N); nmr (CCl_4) τ 5.20 [q (J = 18.2 Hz), CH_2N, 2], 6.35 (s, OCH_3, 3), 6.38 (s, OCH_3, 3), and 7.4–9.1 [m (characteristic peaks at τ 7.47, 7.54, 7.62, 7.70, and 8.30), cyclopentane ring protons, 6].

Dimethyl Bicyclo[2.1.0]pentane-1,4-dicarboxylate (6).—A solution of 10.0 g (47.1 mmol) of pyrazoline **7** in 600 ml of ether was irradiated for 6 hr with a Hanovia 450-W lamp (type L) using a quartz immersion well and a Corex filter. The temperature was kept near 25° by circulating tap water through the jacketed well. Evolution of nitrogen could be observed as the reaction proceeded. Progress of the reaction was followed *via* the nmr spectra of small aliquots. The ether solution was concentrated to a yellow liquid, which was chromatographed on 150 g of neutral, activity 3 alumina with benzene to remove polymer. Trap-to-trap distillation [60–70° (0.001 mm)] of the benzene eluted product from

two 10-g runs gave 9.45 g of liquid. Glpc analysis on a 6 ft × 0.25 in. 10% Carbowax on Chromosorb P column showed the presence of four components. Their retention times and percent compositions were 2.7 (1.7%), 4.0 (5.5%), 5.4 (4.2%), and 6.6 min (88.5%). The first peak was identified as diester **1b** by retention time comparison with that of an authentic sample. The second and third components were collected and their ir and nmr spectra indicated then to be olefinic products of unknown structure. The major component, peak four, was the desired product; however, thermal rearrangement occurred on the glpc column as a collected sample indicated the rearranged product to probably be dimethyl Δ^1- or Δ^5-cyclopentene-1,3-dicarboxylate: ir (thin film) 1720 (C=O) and 1640 cm^{-1} (C=C); nmr (CCl_4) τ 3.40 [m (crude triplet) (J = 3 Hz), vinyl proton, 1], 6.30 (s, OCH_3, 3), 6.32 (s, OCH_3, 3), and 7.2–7.9 (m, 5).

Dimethyl bicyclo[2.1.0]pentane-1,4-dicarboxylate (**6**) was purified by recrystallization from hexane at Dry Ice–acetone bath temperature. Assuming the distilled product to be 88.5% pure, the corrected yield was 51%. Pure material had a melting point between 10 and 20°; ir (thin film) 1730 cm^{-1} (C=O); nmr (CCl_4) τ 6.36 (s, OCH_3, 6), 7.25–7.83 [m (characteristic peaks at τ 7.41, 7.53, and 7.65), exo ring protons, 3], 8.10–8.68 [m (characteristic peaks at τ 8.40, 8.43, and 8.51), endo ring protons, 3]; near-ir (CCl_4) 1.636 μ (ϵ 0.33).

Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.84; H, 6.66.

Photolysis of Dimethyl 2,3-Diazabicyclo[3.3.0]oct-2-ene-1,5-dicarboxylate to Produce Dimethyl Bicyclo[3.1.0]hexane-1,5-dicarboxylate.—Dimethyl 2,3-diazabicyclo[3.3.0]oct-2-ene-1,5-dicarboxylate (8.25 g, 36.4 mmol) (corrected for 5% impurity) was photolyzed using the same conditions as employed above for *dimethyl 2,3-diazabicyclo[3.2.0]hept-2-ene-1,5-dicarboxylate*. After 1.25 hr the nmr spectrum of an aliquot showed no starting material remaining. The product was trap to trap distilled [100° (0.01 mm)], giving 7.29 g of colorless liquid. The product was identified as dimethyl bicyclo[3.1.0]hexane-1,5-dicarboxylate by comparison of its nmr spectrum and of glpc retention times with those of an authentic sample.[2] The distilled product was shown to be 88% pure by glpc analysis, which gave a corrected yield of 84%.

Bicyclo[2.1.0]pentane-1,4-dicarboxylic Acid (8).—To 2.395 g (13 mmol) of **6** dissolved in 20 ml of 80% methanol was added 3.0 g (55 mequiv) of potassium hydroxide in 10 ml of 80% methanol. The mixture was allowed to stand at room temperature for 2 days, concentrated by flash evaporation, diluted to 35 ml with water, acidified to pH 2, and continuously extracted with ether for 10 hr. The ether extract was dried ($MgSO_4$) and concentrated, giving a white solid that produced 1.675 g (82.5%) of product upon recrystallization from ethyl acetate–hexane: mp 169–170° (some decomposition); ir (Fluorolube mull) 2200–3300 (acid OH) and 1700 cm^{-1} (C=O). Reaction of a small portion of this diacid with diazomethane in ether gave the starting diester.

Anal. Calcd for $C_7H_8O_4$: C, 53.85; H, 5.16. Found: C, 54.10; H, 5.34.

4-Carbomethoxybicyclo[2.1.0]pentane-1-carboxylic Acid (9).—A solution of 8.31 g (0.126 equiv) of potassium hydroxide and 50 ml of methanol was added dropwise over a 4-hr period to 23.25 g (0.126 mol) of **6** dissolved in 50 ml of methanol at room temperature. The mixture was stirred for 12 hr, concentrated, and diluted with 50 ml of water. The remaining diester was extracted with ether before saturating the solution with sodium chloride and acidifying to pH 2. The acidified solution was continuously extracted with ether for 10 hr, and the extracts were dried ($MgSO_4$) and concentrated, giving a viscous liquid that crystallized. This material was recrystallized from ether–cyclohexane and sublimed twice [90° (0.01 mm)], giving 15.10 g (67%) of the desired half-ester: mp 71–72°; ir (Fluorolube mull) 2400–3300 (acid OH), 1720 (ester C=O), and 1690 cm^{-1} (acid C=O); nmr (CCl_4) τ −1.3 (s, CO_2H, 1), 6.32 (s, OCH_3, 3), 7.3–8.8 [m (characteristic peaks at τ 7.39 and 7.49), exo ring protons, 3], and 8.0–8.7 [m (characteristic peaks at τ 8.35, 8.39, 8.44, and 8.50), endo ring protons, 3]; mass spectrum (70 eV, direct insert) $M\cdot^+$ at m/e 170.

Anal. Calcd for $C_8H_{10}O_4$: C, 56.47; H, 5.92. Found: C, 56.71; H, 6.00.

Methyl 4-Carbamylbicyclo[2.1.0]pentane-1-carboxylate (10).—A solution of 3.00 g (17.6 mmol) of **9** and 2.6 ml (18.61 mmol) of triethylamine in 40 ml of chloroform was cooled in an ice bath and 1.6 ml (20 mmol) of ethyl chloroformate was added rapidly with stirring. After 15 min anhydrous ammonia was bubbled through the solution (immediate formation of a precipitate) for 1 hr. After standing at room temperature for 3 hr, the mixture was filtered and concentrated, giving a viscous liquid which was crystallized from ether–hexane giving 2.05 g (69%) of the product: mp 81.5–82.5°; ir (Fluorolube mull) 3300 and 3120 (NH), 1725 (ester C=O), 1665 (carbamyl C=O), and 1625 cm^{-1} (carbamyl); nmr ($DCCl_3$) τ 3.5–4.8 (broad m, NH_2, 2), 6.24 (s, OCH_3, 3), 7.4–7.7 (m, 2), 7.7–8.0 (m, 1), and 8.0–8.6 [m (characteristic peaks at τ 8.21, 8.28, 8.31, and 8.43), 3]; mass spectrum (70 eV, direct insert) $M\cdot^+$ at m/e 169.

Anal. Calcd for $C_8H_{11}O_3N$: C, 56.80; H, 6.55. Found: C, 56.98; H, 6.69.

4-Carbamylbicyclo[2.1.0]pentane-1-carboxylic Acid (12).—Ester **10** (0.88 g, 5.2 mmol) was stirred with 1.2 g (21 mequiv) of potassium hydroxide in 50 ml of 80% methanol for 4 hr. The mixture was concentrated and diluted with 25 ml of water. The solution was then washed with ether, acidified, saturated with sodium chloride, and continuously extracted with ether for 2.5 days. The final ether extract was concentrated and the product was recrystallized from ethyl acetate–hexane, giving 0.60g (75%) of the product: mp 179–182° dec; ir (Fluorolube mull) 3450 and 3290 (NH), 2200–2600 (acid OH), 1900 (broad hydrogen-bonded peak), and 1675 cm^{-1} (C=O).

Anal. Calcd for $C_7H_9O_3N$: C, 54.19; H, 5.85; N, 9.03. Found: C, 54.38; H, 5.96; N, 9.15.

Methyl 4-Cyanobicyclo[2.1.0]pentane-1-carboxylate (11).—A solution of 2.00 g (11.8 mmol) of **10** and 5.0 g (33 mmol) of phosphorus oxychloride in 40 ml of ethylene dichloride was stirred at 75–80° for 30 min, after which the evolution of hydrogen chloride could not be observed. The reaction mixture was diluted with chloroform and eluted rapidly over 70 g of neutral, activity 3 alumina with chloroform. Heat was given off as the solution passed down the column. The eluent was trap to trap distilled [80° (0.001 mm)], giving 1.335 g of colorless liquid which was shown by nmr spectroscopy to contain three major methyl ester components. This mixture was chromatographed over 100 g of neutral, activity 2–3 alumina. The desired product began eluting from the column using 85:15 benzene–CCl_4 and trailed in small amounts until methylene chloride eluted the remaining product in fairly pure form. The impurities were not isolated or characterized. The fractions containing the product were combined and distilled using a Hickman still, giving 190 mg of colorless liquid (pure by nmr): ir (thin film) 2225 (C≡N) and 1730 cm^{-1} (C=O); nmr (CCl_4) τ 6.27 (s, OCH_3, 3), 7.3–7.7 (m, 2), 7.7–8.0 (m, 1), and 8.1–8.5 [m (characteristic peaks at τ 8.30 and 8.39), 3].

4-Cyanobicyclo[2.1.0]pentane-1-carboxylic Acid (13).—Ester **11** (190 mg, 1.26 mmol) was hydrolyzed with 0.3 g (5 mequiv) of potassium hydroxide in 15 ml of 80% methanol for 2 hr. The mixture was concentrated, diluted with 20 ml of water, saturated with sodium chloride, acidified to pH 2, and extracted with ether. The ether extract was dried ($MgSO_4$) and concentrated. The residue was recrystallized from ether–hexane, giving 130 mg (75%) of long needles which were further purified by sublimation [80° (0.01 mm)]: mp 112.5–113.5°; ir (Fluorolube mull) 2400–3300 (acid OH), 2220 (C≡N), and 1675 cm^{-1} (C=O).

Anal. Calcd for $C_7H_7O_2N$: C, 61.31; H, 5.14. Found: C, 61.43; H, 5.22.

Bicyclo[2.1.0]pentane-1-carboxylic Acid (15).—Ester **14**[7] (0.870 g, 6.9 mmol) was treated with 1.2 g (21 mequiv) of potassium hydroxide in 20 ml of 80% methanol for 24 hr. The solution was concentrated, diluted with water, acidified, and extracted with ether. The ether extract was dried ($MgSO_4$), and the small amount of product (loss of a good portion due to a laboratory accident on evaporation of the solvent) was distilled [50° (0.001 mm)] using a Hickman still, giving 211 mg (27%) of colorless liquid: ir (thin film) 2400–3300 (acid OH) and 1700 cm^{-1} (C=O); nmr (CCl_4) τ −1.3 (s, CO_2H, 1), 7.2–8.1 (m, 3), and 8.1–8.9 (m, 4).

Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 63.90; H, 7.24.

Registry No.—**1c**, 13368-79-1; **1d**, 4336-19-0; **1e**, 31150-45-5; **2a**, 869-09-0; **2b**, 868-72-4; **2c**, 868-73-5; **2d**, 868-74-6; **2e**, 18281-62-4; **2f**, 34731-71-0; *cis*-**3**, 30630-38-7; *trans*-**3**, 30630-39-8; **6**, 22248-45-9; **7**, 22248-46-0; **8**, 34731-76-5; **9**, 34731-77-6; **10**, 34731-

78-7; **11**, 34731-79-8; **12**, 34731-80-1; **13**, 34731-81-2; **15**, 32811-83-9; dimethyl 1-methoxy-*cis*-cyclopropane-1,2-dicarboxylate, 30630-35-4; dimethyl 1-*tert*-butoxy-*cis*-cyclopropane-1,2-dicarboxylate, 30630-40-1.

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Conformational Analysis. LXXXV. The *cis,cis*-1,6-Cyclodecadiene System[1,2a]

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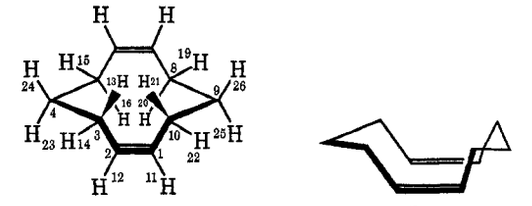
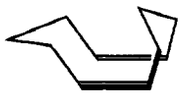
Molecular force field calculations were carried out on *cis,cis*-1,6-cyclodecadiene and on *cis,cis*-cyclodeca-3,8-diene-1,6-dione. The former is calculated to be a 65:35 mixture of chair and boat forms. The bond lengths and angles are in good agreement with the electron diffraction values. The dione is calculated to be a mixture of chair, boat, half-boat in the ratio of 0.59, 0.32, 0.09. Bond lengths and angles are predicted. The dipole moment of the mixture is calculated to be 1.5 D and measured experimentally as 1.4 D. The heats of formation were also calculated.

A great many studies have been reported on the conformational analysis of the 1,6-cyclodecadiene ring system (I) during the past several years.[3-14] These have included a variety of nmr studies of the hydrocarbon itself and a number of derivatives, an electron diffraction study of the hydrocarbon (I) in the gas phase, and an X-ray study of the crystalline dione derivative (II), among others. In each case it was concluded that the chair conformation (Ia, IIa) was the predominant or exclusive structure present.

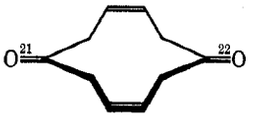


Ia

Ib

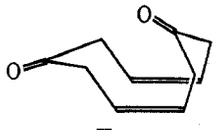


Ic



IIa

IIb



IIc

Earlier papers have described force field calculations which permit us to determine with reasonable accuracy the molecular geometries and conformational energies of various kinds of molecules, including alkanes,[15] alkenes,[1] and ketones.[16] The calculations deal with all of the usual steric effects, torsion, etc., and a classical electrostatic calculation between dipoles is used to allow for interaction between polar groups (double bonds and carbonyl groups).[17]

We have studied the three conformations which models indicate most probable: The chair conformation of symmetry C_{2h} (a), the boat conformation of C_{2v} (b), and a conformation of symmetry C_s (c). We have examined separately the parent hydrocarbons I, and also the diketo derivatives II.

Our calculations give relative energies for Ia, Ib, and Ic of 0.0, 0.34, and 5.01 kcal/mol, respectively. These calculations suggest that the chair conformation (Ia) will predominate over the boat (Ib) by about 65:35 at room temperature, and the amount of the C_s conformation will be negligible. Since the two former structures each have a symmetry number of 2, the predominance of the chair form will increase with a lowering of temperature, and this seems to be consistent with the electron diffraction work. The available experimental nmr work has been interpreted in terms of a single stable conformation (Ia) at low temperatures, which rapidly inverts at higher (room) temperature.

The calculated structure for the chair form is compared with the electron diffraction structure in Table I.

Dale[5,6] has suggested from double bond isomerization studies in some C_6–C_{24} cyclic dienes that in the C_6, C_{10}, and C_{14} ring series the conformation with the cis double bonds diametrically opposed is a "strain-free" one, due to the lack of intramolecular van der Waals contact between ring hydrogens and the double bond

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